Materials for second order nonlinear optics

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CHAPTER 4

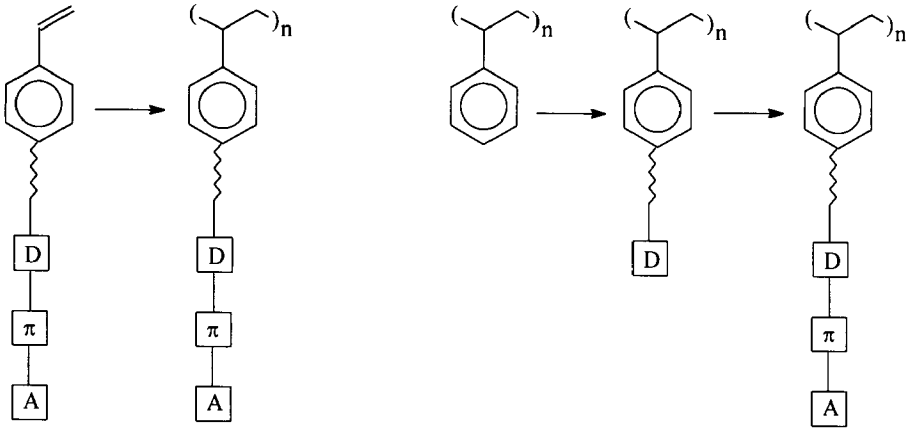
POLYSTYRENE BASED PUSH-PULL AZOBENZENES

4.1 Introduction

Considerable efforts in the area of NLO materials have been focussed on polymer side chain systems (chapter 1.5.2). In this chapter, the synthesis and NLO properties of a polystyrene modified with donor-acceptor units in the side chain are described.
Polystyrene is the most widely used support for all kind of functional groups.[1] The use of polymers other than polystyrene has often met limited success for reasons such as lack of reactivity and degradation of the polymer side chain. The following advantages for the use of polystyrene can be given:

- It undergoes functionalization of the aromatic ring by electrophilic substitution.
- Styrene based polymers are compatible with most organic solvents and functional groups attached to it are easily accessible to reagents and solvents.
- The aliphatic hydrocarbon backbone is chemically relative inert. Hence the polymer chains are not susceptible to degradative scission by most chemical reagents under ordinary conditions.
- Styrene polymers are mechanically stable during handling.

Polystyrene has been used as a matrix to dissolve NLO active compounds in host-guest matrices[2,3] (see chapter 1.4.3), but more interesting materials were developed by linking NLO active units covalently to the polystyrene backbone.
Two approaches for the preparation of polystyrene derivatives are possible (scheme 4.1):
A) Synthesis of functionalized styrene derivatives, followed by (co)polymerization.[4]
B) Functionalization of polystyrene.
We decided to use approach B which has the advantage that the end product is found free of polymerization catalyst and also problems with the reactivity of the already introduced NLO active moieties during the polymerization procedure are excluded. Another important advantage is, that the molecular weight of the polymer is known and other properties such as glass-transition temperature and solubility can be better predicted and/or tuned.
The synthesis of several styrene based polymer side chain systems have been described. Most are prepared according to approach B using poly(*p*-hydroxystyrenes) or poly(*p*-chloromethylstyrenes) as starting materials and chiral *N*-(4-nitrophenyl)-(*S*)-prolinoxy[5], *N*-(*p*-(4-nitrostyryl)-phenyl)-(*S*)-prolinol[6] or Disperse Red 1[7] as covalently linked NLO active units. The orientational stability of the NLO active units in these systems was greatly enhanced by cross-linking with a polyfunctional epoxide reagent during the poling process.[8] All the polystyrene derivatives described above were prepared by introduction of



Scheme 4.1: Two approaches for the synthesis of polystyrene based NLO active materials.

a complete NLO active unit in one step. We decided to use the same strategy as was followed for the amylose derivatives (chapter 3.2):

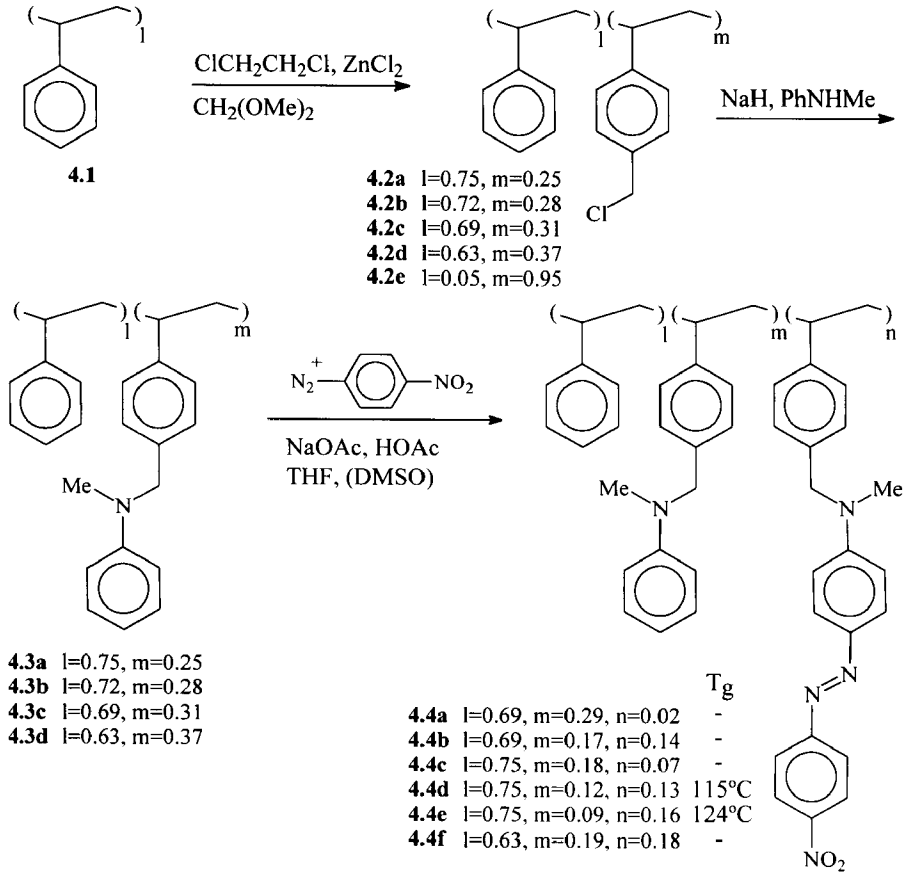
(a) Introduction of a dialkylaminophenyl group as donor functionality.
(b) Diazonium coupling reaction for completing the azobenzene and introduction of the acceptor part.

This synthetic procedure allows variation in the acceptor part using the same donor substituted polystyrene derivative. During this research Wu described a similar procedure for the preparation of electro-optically sensitive polymers.[9] In step b (the diazonium coupling) he used isolated diazonium salts. We were able to use *in situ* formed diazonium salts and avoided the dangerous and sometimes difficult isolation of the salts.[10]

4.2 4-((Methyl-(4-(4-nitrophenylazo)-phenyl)amino)methyl)polystyrene (4.4)

4.2.1 Synthesis of Polystyrene Derivative 4.4

The synthetic route we followed is depicted in scheme 4.2. Polystyrene (Dow Styron 666, Mw = 100,000) (**4.1**) was chloromethylated by a modified Galeazzi method to yield polystyrene derivatives **4.2a-e**.[11] The functionalization degree (DF) of 4-(chloromethyl)-polystyrene (**4.2**) was determined by comparing the integration of chloromethylene protons with the integration of the polystyrene backbone protons in ^{1}H-NMR and/or elemental



*Scheme 4.2: Synthesis of polystyrene derivatives **4.4a-f**.*

analysis and varied between 0.25 and 0.95. The amount of thionyl chloride used in this reaction is an important factor in order to control the resulting DF of the product. Compound **4.2** was treated with the sodium salt of *N*-methylaniline in THF, according to a procedure described in the literature for the coupling of *N*-methylaminopyridine with **4.2**,[12,13,14] providing 4-{(*N*-methyl-*N*-phenylamino)methyl}polystyrene (**4.3**) in good yields (75-87%). Elemental analysis revealed the absence of chlorine in product **4.3**.

The diazonium coupling on polymers **4.3** was carried out using different reaction conditions to provide azopolymers **4.4**. Throughout this chapter the functionalization degrees of **4.4** and **4.6** are denoted by *'l'* for unfunctionalized polystyrene units, *'m'* for 4-{(*N*-alkyl-*N*-phenylamino)methyl}polystyrene units and *'n'* for 4-([alkyl-{4-(4-nitrophenylazo)-phenyl}-amino]methyl)polystyrene units. In procedure A the reaction was performed in a two phase

system consisting of a buffered H_2O/acetic acid layer containing the diazonium salt of *p*-nitroaniline and a THF layer containing the polymer.[10] Using this two phase system the maximum conversion of the aniline moieties to push-pull azobenzenes was 45%. The conversion was determined by UV/Vis (by comparison of the absorption of the **4.4** with the reference compound {4-(4'-nitrophenyl)azo}*N*,*N*-dimethylaniline and/or ^{1}H-NMR spectroscopy by comparing the integration of the methylene protons of the 4-{(*N*-methyl-*N*-phenylamino)methyl} moiety with the 4-([methyl-{4-(4-nitrophenylazo)-phenyl}amino]-methyl) moiety. In procedure B, an anhydrous homogeneous system was used containing THF and DMSO as solvents (chapter 2.2.4) and a maximum conversion of 64% was achieved. The choice of medium in which the diazonium coupling was performed is very important. The solubility of the polymer diminished during the reaction when the conversion increases and conversions higher than 64% could not be achieved due to precipitation of the product during the reaction.
Using these two diazonium coupling conditions, polymers **4.4a-f** were prepared in good yield (63-95%). The functionalization degree 'n' (DF-n) varied between 0.02 (**4.4a**) and 0.18 (**4.4f**). All products were isolated as intense red fibrous solids with a λ_{max} of 478 nm. A clear relationship between DF-n and the solubility of the product was found: An increase of DF-n resulted in a diminished solubility. Compound **4.4f** is only slightly soluble in chloroform and most of this product swelled to form a jelly mixture. During purification of crude **4.4b** and **4.4e** by precipitation from chloroform into methanol, some insoluble jelly material was present also, which was removed by filtration. This is an indication that the limit of solubility is almost achieved with compounds **4.4b** and **4.4e** and this limit is passed with compound **4.4f**.

4.2.2 Optical Characterization of Compound 4.4e[15]

Polystyrene based push-pull azobenzene **4.4e** was used for optical characterization and its poling properties were examined because it is one of the prepared polymers with high DF-n which showed good solubility in chloroform. Thin (1 μm) films were prepared by dipping a substrate in a solution of **4.4e** in chloroform. Poled films were made by applying a positive corona discharge. The poling efficiency, expressed as the order parameter Φ_a ($\Phi_a = (3\langle\cos^2\theta\rangle-1)/2$, was determined by refractive index measurements.[16] The poling induced birefringence, which was measured at 633 nm. Combining this result with the refractive index for the unpoled polymer at 633 nm and the calculated refractive index at infinite wavelength revealed $\Phi_a = 0.45$ (see chapter 1.4.3 for examples of poled polymers with high ordening parameters and high NLO activity). This relative high value can be attributed to the low conductivity of the polymer, resulting in a high effective poling field across the polymer film.

A very important property for integrated optics is the possibility to bleach the polystyrene based NLO active compound **4.4e** irreversibly. The chromophore is completely destroyed after bleaching with a 200 W high pressure Hg lamp. This was shown by the disappearance of the absorption at 490 nm in the UV/Vis spectra after bleaching. The refractive index decreased by a value of 0.05 at 633 nm which allowed the preparation of low loss (±1 dB/cm) channel waveguides by exposure through photomasks in a standard mask aligner. A energy loss of 1 dB/cm of a transmitted signal in a waveguide is a sufficiently low value for use in electro-optical devices.[17]

4.2.3 Electro-Optical Properties of Compound 4.4d[18]

In the previous section it was shown that films of polystyrene based NLO active material such as **4.4e** can be prepared and the dipoles can be aligned by poling, which should result in NLO activity. Besides **4.4e**, compound **4.4d** possesses also a high content of NLO active groups (DF-n = 0.16) in combination with sufficient solubility in chloroform which makes it possible to prepare thin polymer films. The NLO activity of a poled film of **4.4d** was determined by electro-optical measurements. A thin film (0.8 μm) of **4.4d** was prepared by spin coating from chloroform and poled by contact poling. After a poling time of 15 min an electro-optical activity of r_{33} = 18.2 pm/V was measured (see chapter 1.5 for explanation of r_{33}). Switching off the field resulted in an instantaneous decrease of r_{33} to 12.9 pm/V. This value corresponds to a $\chi^{(2)}(\omega,\omega,o)$ = 60 pm/V which is measured at 633 nm and not off resonance. Using the two-level model (chapter 1.6) a corrected value at an off resonance value can be calculated giving $\chi^{(2)}(\omega,\omega,o)$ = 21.2 pm/V at 1.52 μm. The ordening Φ_b (Φ_b = 1-$\langle\cos^3\theta\rangle$) of the NLO active units was calculated using the second hyperpolarizability (β). The β was assumed to be equal to a value of a similar azo dye: Disperse Red 19.[19] Φ_b appeared to be 0.43 and is almost identical to the Φ_a of a Corona poled film of **4.4e**, that was calculated using refractive index measurements.

The stability of the poled films at different temperatures is shown in figure 4.1. Storing poled films at 80°C results in a relaxation to 40-50% of the initial value after about one month. At 50°C the relaxation stabilizes at about 75% of the initial value and at room temperature at a value of about 90% of the original value ($\chi^{(2)}(\omega,\omega,o)$ = 60 pm/V). Upon storage at higher temperatures (100°C), the relaxation is very fast and the ordening is lost within days. It can be concluded that the thermal stability of poled films of **4.4e** is sufficient at temperatures up to 50°C, but at higher temperatures a loss of 50% or more of the initial value within months is observed. Therefore these polymers are less suitable for application in integrated optics, because it is expected that stability up to temperatures of 100°C are necessary for such applications. As already described in chapter 1, stability to relaxation

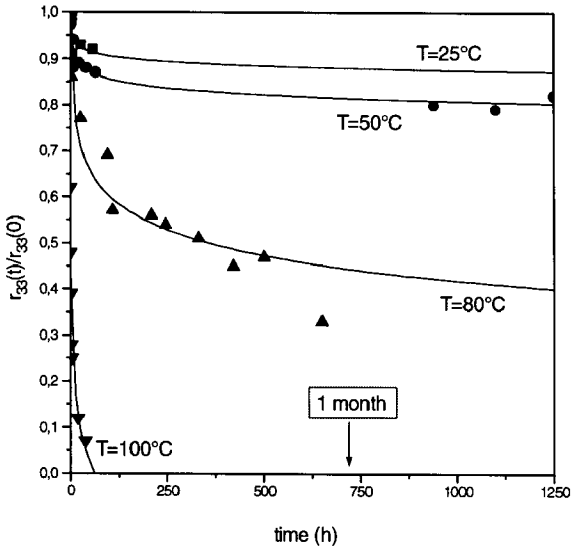


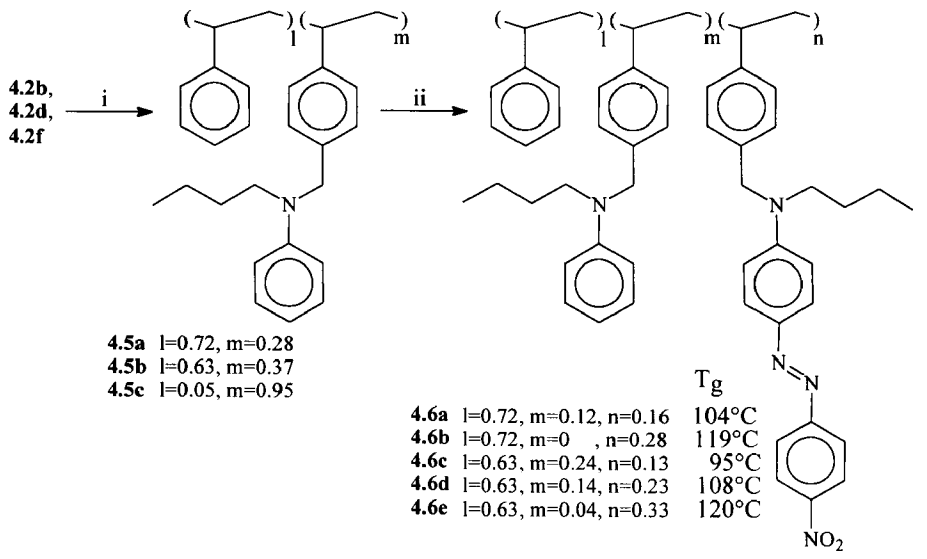
Figure 4.1: Isothermal decay of ***4.4e*** *determined by electro-optical measurements (r_{33}) at T = 25°C (●), at T = 50°C (■), at T = 80°C (▲) and at T = 100°C (▼).*

at 100°C requires a T_g of the polymer of at least 160°C. Sixty degrees difference between T_g and storage temperature is normally efficient in order to retain ordening for a long time. This value of 60 degrees corresponds to the observed stability of **4.4e** up to 50°C (65°C below T_g).

4.3 Substitution of the *N*-Methyl Group for an *N*-*n*-Butyl Group

A number of favorable properties for polystyrene based NLO active compound **4.4** are found so far: - High ordening after poling
- Good film forming properties
- Preparation of waveguides by irreversible bleaching

However, still some improvements, such as slower isothermal decay and higher NLO activity, are desired. Polymers with a higher T_g will show slower relaxation.[20] The NLO activity might be improved by increasing the content of NLO active units in the polymer. The solubility of **4.4** showed to be a limiting factor for the enhancement of the number of NLO active units. To overcome this problem we introduced *n*-butyl group at the donor nitrogen (scheme 4.3). It was expected that the introduction of a longer alkyl chain will enhance the solubility. The same synthetic procedure as for the *N*-methyl analogs was



Scheme 4.3: Synthesis of N-n-butyl containing polystyrene derivatives ***4.6a-e****. Reaction conditions: (i) NaH, PhNH-n-C_4H_9, (ii) p-nitroaniline, $NaNO_2$, H_2SO_4, NaOAc/HOAc, DMSO, THF.*

followed, but instead of *N*-methylaniline, *N-n*-butylaniline was used providing polystyrene derivatives **4.5a-b** in good yields (90-91%). Polymer **4.5c** showed poor solubility because of the high functionalization degree (DF-m) and was isolated in low yield (30%). Compound **4.5c** could not be dissolved in a medium suitable for the diazonium coupling procedure and no conversion to D-π-A systems was achieved. Polystyrene derivatives **4.5a** and **4.5b** showed sufficient solubility and were used for a diazonium coupling (scheme 4.3). Polymers **4.6a-e** were prepared in moderate to good yields (63-90%) as intense red colored fibrous solids. The conversions varied between 35% and 100%, *i.e.* DF-n, determined by ^{1}H-NMR, varied between 0.13 and 0.33 (see chapter 4.2.1). The introduction of a *n*-butyl group at the donor nitrogen provided the possibility to double the content of NLO active units from DF-n = 0.16 (**4.4e**) to DF-n = 0.33 (**4.6e**), *i.e.* one third of all styrene units is modified to a D-π-A system. By using **4.5a** for the diazonium coupling reaction, complete conversion of the donor groups was achieved to afford polymer **4.6b**. With **4.6b** and **4.6e** the limit of solubility was achieved as was shown by the fact that both crude products were not completely soluble but a solution in chloroform contained jelly particles.

The T_g's of polystyrene derivatives **4.6** were lower than the T_g's of the *N*-methyl derivatives **4.4** with similar content of D-π-A systems. Comparing the T_g's of compounds **4.4e** and **4.6a**, containing equal dye amounts, revealed that the substitution of a *N*-methyl for a *N*-*n*-butyl group lowers the T_g with about 20°C. An increase of the content of NLO active units results in a higher T_g. This effect neutralizes the decrease due to the presence of a *n*-butyl group, but the resulting T_g is still too low for good ordening stability at temperatures above 50°C.

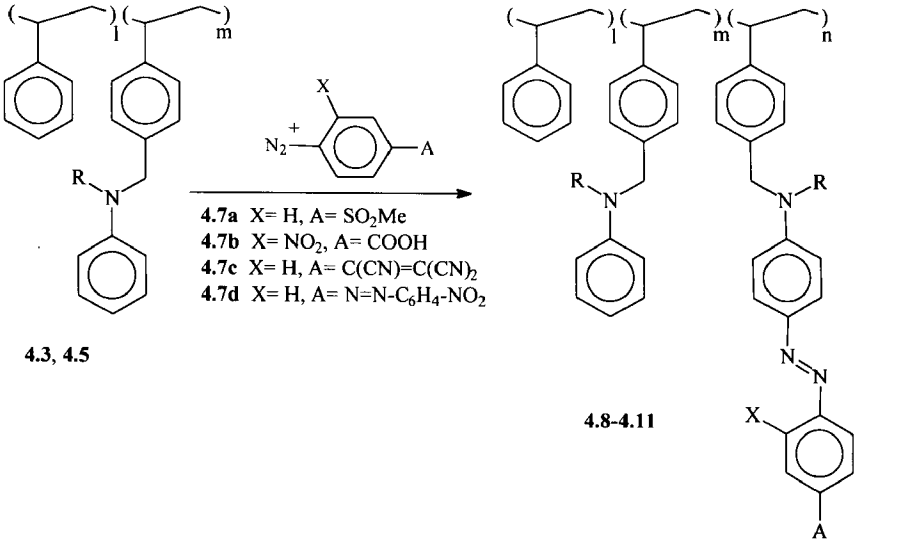
4.4 Variation in Acceptor Functionality

In the case of polystyrene based NLO active compounds **4.4** and **4.6** we introduced the widely used NO_2-acceptor group. Inherent to the synthetic route used for the preparation of **4.4** and **4.6**, it is easy to vary the acceptor functionality using different substituted diazonium salts derived from aniline derivatives (**4.6a-c**). It is known that no material has proven to be the 'silicon' of nonlinear optics and each material has properties that are advantageous for certain applications.[21] Therefore, it is important to have the possibility to prepare a wide variety of materials in an easy way.

For example, azobenzene based materials with a alkylsulfonyl group as acceptor functionality show a hypsochromic shift of the λ_{max} compared with their nitro analogs and are therefore suitable for frequency doubling of light with a wavelength of 820 nm.[22] In order to introduce a methylsulfonylbenzene acceptor unit, the diazonium coupling of **4.3a** with *p*-(methylsulfonyl)aniline was examined. Using 1 equivalent of diazonium salt for each *N*-methylaniline unit of **4.3a**, a conversion of 20% (determined by ^{1}H-NMR) was reached yielding compound **4.8** with a DF-n of 0.05 (scheme 4.4). Polystyrene derivative **4.8** was isolated as a badly soluble orange colored solid. The color indicates a hypsochromic shift to lower wavelengths compared to the nitro derivatives.

The diazonium salt of 4-amino-3-nitrobenzoic acid (**4.7b**) gave a very efficient reaction with polystyrene **4.3c** using procedure B (chapter 4.2.1). The use of a 5-fold excess of this diazonium salt resulted in 100% conversion (determined by ^{1}H-NMR) yielding polystyrene derivative **4.9** with a DF-n of 0.31 as a very dark colored compound. Compound **4.9** was soluble in DMSO and NMP, but no thin polymer films, suitable for poling and NLO activity measurements, could be formed.

The second hyperpolarizability (β) of the NLO active unit of **4.9** and the β's of the NLO active units of derivatives **4.4** and **4.6** have been reported to be approximately equal.[23] Compound **4.6e**, for example, with a similar content of NLO active units and better film forming properties is therefore more interesting for further investigation.

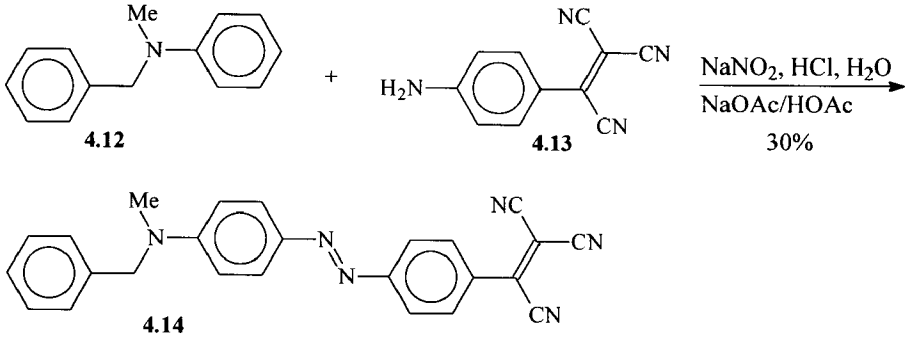


Comp.	R	A	X	l	m	n	solubility	T_g
4.8	Me	SO_2Me	H	0.75	0.20	0.05	$CHCl_3$	-
4.9	Me	COOH	NO_2	0.63	0	0.37	DMSO/NMP	-
4.10	n-Bu	$C(CN)=C(CN)_2$	H	0.75	0.17	0.08	slightly $CHCl_3$	88°C
4.11	n-Bu	$N=N-C_6H_4-NO_2$	H	-	-	-	not soluble	-

Scheme 4.4: Synthesis of polystyrene derivatives with different acceptors.

4.4.1 Tricyanoethenyl as Acceptor

As already mentioned in previous sections, despite all interesting properties reached so far, the NLO activity of polystyrenes **4.4d-e** is still not sufficiently high for use in applications. Substitutions of the nitro group for a stronger acceptor would increase the β of the NLO active unit.[19] A very strong acceptor is the tricyanoethenyl group[24,25] which may be introduced at the polystyrene backbone using the diazonium salt of *p*-(tricyanoethenyl)-aniline (**4.7c**, scheme 4.4).[26] Schilling *et al.* described a diazonium coupling on different donor substituted aromatic substrates with the isolated diazonium salt of *p*-(tricyanoethenyl)aniline (BF_4^- or PF_6^- as counter ion).[27] However, the preparation of this salt failed in our hands and it was decided to use the *in situ* formed diazonium salt. The reactivity of the diazonium salt of *p*-(tricyanoethenyl)aniline (**4.7c**) was tested on monomeric system model compound **4.12** (scheme 4.5).

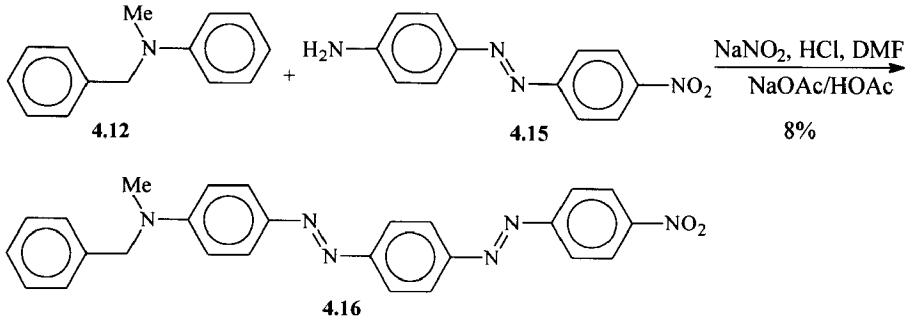


*Scheme 4.5: Synthesis of (tricyanoethenyl)azobenzene derivative **4.14**.*

N-Benzyl-*N*-methylaniline (**4.12**), a monomeric analog of polystyrene derivative **4.3** was used for a diazonium coupling with **4.13** under standard conditions (see chapter 2.2.4, procedure A). Compound **4.14** was isolated in 30% yield proving the *in situ* formed diazonium salt of **4.13** to be reactive. A similar reaction with polystyrene derivative **4.5a** yielded a black polymer **4.10** (scheme 4.4) which showed poor solubility. The crude product was slightly soluble in chloroform, allowing an estimation of the conversion using ^{1}H-NMR spectroscopy. It was shown that about 26% of the aniline moieties were converted, *i.e.* DF-n = 0.08. Due to this low conversion a low T_g of 88°C of polymer **4.10** was found. Unfortunately, further handling of polystyrene derivative **4.10** was impossible due to its poor solubility.

4.4.2 Push-Pull Bis-Azobenzenes

Amano and Kaino have described that elongation of a push-pull azobenzene to a push-pull bis-azobenzene results in a much higher second order hyperpolarizability (β).[28,29] The β is increased with a factor 2.5 when an azobenzene with NR_2 as donor and NO_2 as acceptor is elongated to a bis-azobenzene with the same substituents.[30] The synthesis of a methacrylate based bis-azobenzene was described by Amano and Kaino.[29] They used a diazonium coupling reaction of an *in situ* prepared diazonium salt of 4-amino-4'-nitroazobenzene (**4.7d**) with an *N*-alkylated-aniline. This procedure is similar to the synthetic route for polystyrene based push-pull azobenzenes described in the previous sections 4.2 and 4.3. Following this procedure it was tried to introduce a push-pull bis-azobenzene on polystyrene in order to improve the NLO activity of the polystyrene derivatives.



Scheme 4.6: Synthesis of bis-azobenzene derivative ***4.16****.*

A diazonium coupling reaction with 4-amino-4'-nitroazobenzene (**4.15**) was first tested on a monomeric system (**4.11**) (scheme 4.6). Pure push-pull bis-azobenzene **4.16** was isolated as a very intensely red colored solid in 8% yield. The low yield was due to the difficult formation of the diazonium salt of 4-amino-4'-nitroazobenzene (**4.15**), which showed to be an very insoluble reagent. The insolubility probably was the main reason for the low yield. Despite the unsatisfactory yield, a diazonium coupling of **4.15** on polystyrene derivative **4.5a** was performed (scheme 4.4). During addition of the *in situ* formed diazonium salt **4.7d** the product (**4.11**) precipitated immediately. The precipitate could not be dissolved in any organic solvent and therefore characterization was not possible. It seems that even at very low conversion polymer **4.11** (scheme 4.4) becomes insoluble. Hence, even a low content of bis-azobenzene units makes the polystyrene derivative useless for the preparation of thin films.

4.5 Concluding Remarks

We succeeded to prepare a wide variety of polystyrene based push-pull azobenzenes in three steps with polystyrene as starting material. The *N*-methyl derivatives **4.4d** and **4.4e** with NO_2 as acceptor, showed the following attractive properties for application in integrated optics:

- Both show good solubility in different solvents.
- It is easy to prepare clear films.
- Thin films of **4.4d-e** show excellent ordening after poling.
- The polymers can be irreversible bleached.

Two improvements are still desired:

- A higher T_g in order to achieve better stability at higher storage temperatures.
- Higher NLO activity.

Modifications in order to reach these goals conflicted, however, with the solubility of polystyrene derivatives. Better NLO activity should be achieved by increasing the content of NLO active units, but such increase resulted in insoluble polymers. The introduction of a *N*-*n*-butyl group resulted in better solubility and a higher content of NLO active units, but simultaneously a decrease of T_g was observed. The introduction of a stronger acceptor, in order to get NLO active units with a higher β, resulted in poor soluble polymers even at low degree of functionalization.

4.6 Experimental section

General Remarks: See chapter 2.7.
Refractive index measurements: (Performed by Diemeer *et al.*[15]) Films of **4.4d** with a thickness of 1 μm were prepared by dipping a substrate in a concentrated solution of **4.4d** in $CHCl_3$. Poling of films of **4.4d** was performed by positive corona discharge (3kV) for 4 h at 112°C (12°C below T_g). Refractive index measurements were performed as described by Diemeer *et al.*[15]
Electro-optical measurements: The EO-measurements were performed by P.T.A. Klaase (TNO). The films of **4.4e** with thickness of 0.8 μm were prepared by spin coating from $CHCl_3$ onto ITO-glass. Poling was done by contact polarization in a field of 500 kV/cm at T_g (**4.4e** at 159°C) for 15 min. Electro-optical measurements were performed at 633 nm with a experimental set up described by Klaase.[18]
Compounds **4.7a**[31], **4.12**[32] and **4.13**[26] were prepared according to literature procedures.
Part of the synthetic work was performed by B. de Lange and E.M. Veen.

4-(Chloromethyl)styrene, styrene copolymer (4.2)[11]
Polystyrene **2.1** (10 g, 95 mmol monomeric units) was dissolved in 1,2-dichloroethane (1 L) and heated to 40°C. A solution of $ZnCl_2$ (13 g, 95 mmol) in methylal (85 mL) was added and the mixture was stirred for 5 min. Subsequently $SOCl_2$ (20 mL, 100 mmol) was added dropwise during 30 min. The resulting red mixture was stirred for another 4 h at 40°C and precipitated in MeOH (5 L). The precipitate was collected, dissolved in $CHCl_3$ (300 mL) and again precipitated in MeOH (1 L). The precipitation procedure was repeated and after drying under reduced pressure **4.2b** (8.3 g, 70%) was isolated as a white fibrous solid.
^{1}H-NMR (200 MHz): δ 1.42 (s, C$\underline{H}_2$-backbone), 1.80 (s, C$\underline{H}$-backbone), 4.51 (s, C$\underline{H}_2$Cl), 6.24-7.25 (m, aromatic $\underline{H}$'s), all signals are broad, integration revealed DF = 0.27 (0.28 according to elemental analysis); IR (KBr): υ 2921, 1601, 1493, 1452, 1265, 757, 698, 679; Anal. calcd for $C_{8.28}H_{8.28}Cl_{0.28}$: C, 84.48; H, 7.09; Cl, 8.43. Found: C, 84.63; H, 7.21; Cl 8.40.
Following the same procedure and varying the amount of $SOCl_2$ (1-4.5 equiv. with respect to **4.1**), compound **4.2** was prepared with different functionalization degrees (determined by ^{1}H-NMR): **4.2a** (DF = 0.25), **4.2c** (DF = 0.31), **4.2d** (DF = 0.37), **4.2e** (DF = 0.95). All products showed similar IR and NMR data and were isolated in yields varying between 70 and 90%

4-{(*N*-Methyl-*N*-phenylamino)methyl}styrene, styrene copolymer (4.3)

NaH (1.1 g, 60% in mineral oil, 27.5 mmol) was washed with *n*-hexane in a dry N_2-atmosphere. THF (150 mL) was added and subsequently freshly distilled *N*-methylaniline (2.7 g, 25 mmol) was added dropwise and the mixture was stirred for 30 min. The formed yellow suspension was heated at reflux for 15 min and subsequently cooled to room temperature. Then a solution of **4.2b** (2.1 g, 17.9 mmol monomeric units, 5 mmol Cl equiv.) in THF (70 mL) was added dropwise and the resulting solution was stirred for 16 h at room temperature. The mixture was precipitated in MeOH (1.5 L), collected and dried. The crude product was dissolved in $CHCl_3$ (100 mL), precipitated in MeOH (700 mL), collected and dried to give **4.3b** (2.33 g, 95%) as a white fibrous solid.
^{1}H-NMR (200 MHz): δ 1.36 (s, C$\underline{H}_2$-backbone), 1.82 (s, C$\underline{H}$-backbone), 2.92 (s, NC$\underline{H}_3$), 4.38 (s, NC$\underline{H}_2$), 6.21-7.30 (m, aromatic $\underline{H}$'s), all signals are broad, DF = 0.28; IR (KBr): υ 2922 (C-H), 1598 (aromatic), 1505, 747 and 698 (aromatic); Anal. calcd for $C_{10.24}H_{10.52}N_{0.28}$: N, 2.85. Found: N, 3.21, Cl<0.03.

4.3a was prepared using **4.2b** as starting material in 74% yield with DF = 0.25.

4.3c was prepared using **4.2c** as starting material in 77% yield with DF = 0.31.

4.3d was prepared using **4.2d** as starting material in 81% yield with DF = 0.37

Compounds **4.3a,c,d** showed ^{1}H-NMR and IR data similar to **4.3b**.

4-([*N*-Methyl-{4-(4-nitrophenylazo)-*N*-phenyl}amino]methyl)styrene,4-{(*N*-methyl-*N*-phenyl-amino)methyl}styrene, styrene copolymer (4.4)

Procedure A:

Compound **4.3c** (2.5 g, 17.7 mmol molecular units, 5.5 mmol *N*-methylaniline equiv.) was dissolved in THF (200 mL) and subsequently were added glacial acetic acid (75 mL) and NaOAc (8.2 g, 100 mmol). The diazonium salt of *p*-nitroaniline was prepared by addition of a solution of $NaNO_2$ (1.6 g, 23 mmol) in H_2O (10 mL) to a solution of *p*-nitroaniline (3.17 g, 23 mmol) in 10 N HCl (9 mL) at 0°C followed by stirring for 30 min. The diazonium salt emulsion (5 fold excess) was added dropwise to the polymer solution at 10°C and the solution was stirred for another 3 h at room temperature. The reaction mixture was poured in MeOH (1 L) and the red precipitate was collected and dried. The crude product was dissolved in $CHCl_3$ (250 mL) (insoluble jelly particles were removed by filtration). The solution was concentrated to about 50-75 mL and precipitated in MeOH (500 mL). The precipitate was collected and dried in vacuum to give **4.4b** (1.8 g, 63%).
^{1}H-NMR (300 MHz): δ 1.35 (s, C$\underline{H}_2$-backbone), 1.75 (s, C$\underline{H}$-backbone), 2.88 (s, NC$\underline{H}_3$, nc*), 3.03 (s, NC$\underline{H}_3$, azo**), 4.35 (s, NC$\underline{H}_2$, nc*), 4.47 (s, NC$\underline{H}_2$, azo**), 6.22-7.20 (m, aromatic $\underline{H}$'s), 7.85 (s, aromatic $\underline{H}$'s), 8.23 (s, aromatic $\underline{H}$'s), all signals are broad, *) nc=not converted and connected to a *N*-phenylamine unit, **) azo=converted and connected to an azobenzene unit; IR (KBr): υ 2921, 1600, 1506, 1338, 1138, 1105, 748, 698; UV/Vis: λ_{max}=477 nm, (ϵ=3.15·10^3, revealed a conversion of 44%: l=0.69, m=0.17, n=0.14); Anal. calcd for $C_{11.32}H_{11.21}N_{0.73}O_{0.28}$: C, 83.94; H, 6.98; N, 6.31. Found: C, 81.82; H, 6.77; N, 7.26.

Procedure B:

Compound **4.3a** (1 g, 7.47 mmol monomeric units, 1.87 *N*-methylaniline equivalents) was dissolved in THF (25 mL) and this solution was added to a solution of NaOAc (1 g, 12 mmol) in

glacial acetic acid (4 mL, 67 mmol) and DMSO (5 mL). $NaNO_2$ (124 mg, 1.80 mmol) was added in small portions to 96% H_2SO_4 (1 mL), *p*-nitroaniline was added and the mixture was stirred for 1 h at room temperature. After cooling to 0°C, 5 mL DMSO was added. The resulting diazonium salt solution was added slowly to the buffered polymer solution and the resulting mixture was stirred for 5 h at room temperature. The reaction mixture was precipitated in 0.5 N NaOH (200 mL) and MeOH (100 ml). The precipitate was collected, washed with water and MeOH and dried. The crude product was dissolved in $CHCl_3$ (30 mL) and precipitated in MeOH (300 mL). The solid was collected and dried in vacuum to give **4.4d** (1.08 g, 95%) as a red fibrous solid.
DSC: Tg=115°C; ^{1}H-NMR (300 MHz): similar as was found for **4.4d**, conversion is 52%; l=0.75, m=0.12, n=0.13; IR data are similar to that of **4.4d**; Anal. calcd for $C_{10.78}H_{10.64}N_{0.64}O_{0.26}$: C, 84.45; H, 6.99; N, 5.85. Found: C, 82.67; H, 7.06; N, 6.20.
Polymer **4.4a** was prepared following procedure A using **4.3c** as starting material and a 2.5 fold excess of the diazonium salt of *p*-nitroaniline. UV/Vis: similar as was found for **4.4d**, conversion is 6%; l=0.69, m=0.29, n=0.02; IR data similar as was found for **4.4d**.
Polymer **4.4c** was prepared in 74% yield following procedure B using **4.4a** as starting material and 0.5 equiv. of the diazonium salt of *p*-nitroaniline. ^{1}H-NMR: similar as was found for **4.4d**, conversion is 28%; l=0.75, m=0.18, n=0.07; IR and UV/Vis data are similar as was found for **4.4d**.
Polymer **4.4e** was prepared in 81% yield following procedure B with **4.3a** as starting material and 2 equiv. diazonium salt of *p*-nitroaniline. DSC: T_g=124°C; ^{1}H-NMR: similar as was found for **4.4d**, conversion is 64%; l=0.75, m=0.09, n=0.16;
Polymer **4.4f** was prepared following procedure B with **4.3d** as starting material and 1 equiv. of the diazonium salt of *p*-nitroaniline. Crude **4.4f** was isolated in 95% yield (purification was not possible due to poor solubility). ^{1}H-NMR similar as was found for **4.4d**, conversion is 49%; l=0.63, m=0.19, n=0.18.

4-{(*N*-*n*-Butyl-*N*-phenylamino)methyl}styrene, styrene copolymer (4.5)
The same procedure as for **4.3b** was followed using **4.2b** and freshly distilled *N*-*n*-butylaniline as starting materials to provide **4.5a** as a white fibrous solid in 91% yield.
^{1}H-NMR (200 MHz): δ 0.92 (s, C$\underline{H}_3$), 1.16-1.97 (m, C$\underline{H}$-backbone, C$\underline{H}_2$-backbone, 2xC$\underline{H}_2$-butyl), 3.29 (s, $CH_2C\underline{H}_2N$), 4.37 (s, ArC$\underline{H}_2$N), 6.17-7.23 (m, aromatic $\underline{H}$'s), all signals are broad, revealed a DF = 0.26 (DF starting material is 0.28); Anal. calcd for $C_{11.08}H_{12.20}N_{0.28}$: C, 89.14; H, 8.24; N, 2.63. Found: C, 88.48; H, 8.35; N, 2.79.
Compound **4.5b** was prepared using **4.2b** as starting material in 90% yield. ^{1}H-NMR: similar as was found for **4.5a**, DF = 0.36 (DF starting material is 0.37); Anal. calcd for $C_{12.07}H_{13.35}N_{0.37}$: C, 88.61; H, 8.22; N, 3.17. Found: C, 88.51; H, 8.52; N, 3.55.
Compound **4.5c** was prepared using **4.2f** as starting material in 30% yield (material was lost due to poor solubility). ^{1}H-NMR: similar as was found for **4.5a**, DF = 0.88 (DF starting material is 0.95).

4-([*N*-*n*-Butyl-{4-(4-nitrophenylazo)-*N*-phenyl}amino]methyl)-styrene, 4-{(*N*-*n*-butyl-*N*-phenyl-amino)methyl}styrene, styrene copolymer (4.6)

Procedure B (see synthetic procedure of **4.4**) was followed using **4.5a** as starting material and 1.5 equiv. of the diazonium salt of *p*-nitroaniline. Compound **4.6a** was isolated in 93% yield as a red fibrous solid.

DSC: T_g=104°C; ^{1}H-NMR (200 MHz, 50°C: δ 0.93 (s, C$\underline{H}_3$), 1.18-1.97 (m, C$\underline{H}$-backbone, C$\underline{H}_2$-backbone, 2xC$\underline{H}_2$-butyl), 3.27 (s, CH$_2$C$\underline{H}_2$N, nc*), 3.38 (s, CH$_2$C$\underline{H}_2$N, azo**), 4.36 (s, ArC$\underline{H}_2$N, nc*), 4.48 (s, ArC$\underline{H}_2$N, azo**), 6.23-7.20 (m, aromatic $\underline{H}$'s), 7.83 (s, aromatic $\underline{H}$'s), 8.25 (s,aromatic $\underline{H}$'s), all signals are broad, conversion is 58%; l=0.69, m=0.17, n=0.13, *) nc=not converted and connected to a *N*-phenylamine unit, **) azo=converted and connected to an azobenzene unit.

Polymer **4.6b** was prepared in 90% yield following procedure B with **4.5d** as starting material and 4 equiv. of the diazonium salt of *p*-nitroaniline. DSC: T_g=119°C; ^{1}H-NMR: similar as was found for **4.6a** (signals missing: δ 3.27 (s, CH$_2$C$\underline{H}_2$N, nc*), 4.36 (s, ArC$\underline{H}_2$N, nc*)), conversion is 100%; l=0.72, m=0.0, n=0.28.

Polymer **4.6c** was prepared in 78% yield following procedure B with **4.5b** as starting material and 1 equiv. of the diazonium salt of *p*-nitroaniline. DSC: T_g=95°C; ^{1}H-NMR: similar as was found for **4.6a**, conversion is 35%; l=0.63, m=0.24, n=0.13.

Polymer **4.6d** was prepared in 63% yield following procedure B with **4.5b** as starting material and 1.5 equiv. of the diazonium salt of *p*-nitroaniline. DSC: Tg=108°C; ^{1}H-NMR: similar as was found for **4.6a**, conversion is 56%; l=0.63, m=0.14, n=0.23.

Polymer **4.6e** was prepared in 67% yield following procedure B with **4.5b** as starting material and 3 equiv. of the diazonium salt of *p*-nitroaniline. DSC: Tg=120°C; ^{1}H-NMR: similar as was found for **4.6a**, conversion is 90%; l=0.69, m=0.04, n=0.33.

4-([*N*-Methyl-{4-(4-methylsulfonylphenylazo)-*N*-phenyl}amino]methyl)styrene, 4-{(*N*-methyl-*N*-phenylamino}methyl)styrene, styrene copolymer (4.8)

Procedure B (see synthetic procedure of **4.4**) was followed using **4.3a** and 1 equiv. of the diazonium salt of *p*-(methylsulfonyl)aniline (**4.7a**) as starting materials. Polymer **4.8** was isolated in 96% yield as an orange solid.

^{1}H-NMR: δ 1.41 (s, C$\underline{H}_2$-backbone), 1.79 (s, C$\underline{H}$-backbone), 2.88 (s, NC$\underline{H}_3$, nc*), 3.04 (s, NC$\underline{H}_3$, azo**), 4.37 (s, NC$\underline{H}_2$, nc*), 4.50 (s, C$\underline{H}_3$N, azo**), 6.23-7.28 (m, aromatic $\underline{H}$'s), 7.85-8.08 (m, aromatic $\underline{H}$'s), all signals are broad, conversion is 20%, l=0.75, m=0.20, n=0.05. *) nc=not converted and connected to a *N*-phenylamine unit, **) azo=converted and connected to an azobenzene unit.

4-([*N*-Methyl-{4-(4-carboxyl-2-nitrophenylazo)-*N*-phenyl}amino]methyl)styrene, 4-{(*N*-methyl-*N*-phenylamino)methyl}styrene, styrene copolymer (4.9)

Procedure B (see synthetic procedure of **4.4**) was followed using **4.3d** and 5 equiv. of the diazonium salt of 4-amino-3-nitrobenzoic acid (**4.7b**) as starting materials. Purification by precipitation from DMSO in MeOH afforded **4.9** in 68% yield as a dark red powder.

^{1}H-NMR (300 MHz, DMSO-d6): δ 1.39 (s, C$\underline{H}_2$-backbone), 1.74 (s, C$\underline{H}$-backbone), 2.98 (s, NC$\underline{H}_3$), 4.49 (s, NC$\underline{H}_2$), 6.21-7.15 (m, aromatic $\underline{H}$'s), 7.69 (s, 3$\underline{H}$), 8.16 (s, 1$\underline{H}$), 8.35 (s, 1$\underline{H}$), COO$\underline{H}$ is missing, all signals are broad, conversion is 100%, l=0.69, m=0, n=0.31.

4-{(*N*-*n*-Butyl-[4-{4-(1,2,2-tricyanoethenyl)phenylazo}-*N*-phenyl]amino)methyl}styrene, 4-{(*N*-*n*-butyl-*N*-phenylamino)methyl}styrene, styrene copolymer (4.10)
Procedure B (see synthetic procedure of **4.4**) was followed using **4.5a** and 1.2 equiv. of the diazonium salt of *p*-(tricyanoethenyl)aniline (**4.7c**) as starting materials. Crude **4.10** was isolated in 73% yield as a black solid that could not be purified due to poor solubility.
DSC: T_g=88°C; ^{1}H-NMR: δ 0.92 (s, C$\underline{H}_3$), 1.15-2.18 (m, C$\underline{H}$-backbone, C$\underline{H}_2$-backbone, 2xC$\underline{H}_2$-butyl), 3.29 (s, $CH_2C\underline{H}_2N$, nc*), 3.42 (s, $CH_2C\underline{H}_2N$, azo**), 4.38 (s, $ArC\underline{H}_2N$, nc*), 4.50 (s, $ArC\underline{H}_2N$, azo**), 6.20-7.23 (m, aromatic $\underline{H}$'s), 7.87 (s, aromatic $\underline{H}$'s), 8.16 (s, aromatic $\underline{H}$'s), all signals are broad, conversion is 26%, l=0.75, m=0.17, n=0.08, *) nc=not converted and connected to a *N*-phenylamine unit, **) azo=converted and connected to an azobenzene unit.

Attempted synthesis of 4-{(*N*-*n*-butyl-[4-{4-(4-nitrophenylazo)phenylazo}-*N*-phenyl]amino)-methyl}styrene, 4-{(*N*-*n*-butyl-*N*-phenylamino)methyl}styrene, styrene copolymer (4.11)
The same procedure as described for **4.16** was followed using **4.5a** and 1 equiv. **4.15** as starting materials. Immediately after addition of a small portion of the *in situ* prepared diazonium salt of **4.15** a polymeric product precipitated. The precipitate was collected, washed with H_2O, MeOH and dried yielding **4.11**. Crude **4.11** showed to be insoluble in $CHCl_3$, DMSO and DMF.

2-[4-{4-(*N*-Benzyl-*N*-methylamino)-phenylazo}-phenyl]-3-cyano-but-2-enedinitrile (4.13)
p-(Tricyanoethenyl)aniline (**4.13**) (300 mg, 1.5 mmol) was dissolved in 5 N HCl (2 mL). The solution was cooled to 0-5°C and $NaNO_2$ (110 mg, 1.6 mmol) was added in portions. The resulting mixture was added to a solution of **4.12** (315 mg, 1.6 mmol) and NaOAc (2.6 g, 32 mmol) in glacial acetic acid (9 mL) and stirred for 3 h at room temperature. The mixture was poured in H_2O (50 mL) and the precipitate was collected and dried. The crude product was purified by column chromatography (CH_2Cl_2) giving **4.14** (180 mg, 30%) as a black solid.
^{1}H-NMR (200 MHz): δ 3.23 (s, 3H), 4.73 (s, 2H), 6.83 (d, J=9.0, 2H), 7.18-7.36 (m, 5H), 7.91 (d, J=9.0, 2H), 7.98 (d, J=9.0, 2H), 8.18 (d, J=9.0, 2H); IR (KBr): υ 2911, 2224, 1596, 1581, 1519, 1374, 1142, 837, 725; UV/Vis: λ_{max}= 596 nm.

***N*-Benzyl-*N*-methyl-[4-{4-(4-nitrophenylazo)-phenylazo}-phenyl]amine (4.16)**
To a solution of $NaNO_2$ (300 mg, 4.3 mmol) in 10 N HCl (5 mL) was added a solution of 4-amino-4'-nitroazobenzene **4.15** (900 mg, 3.7 mmol) in DMF (40 mL) at 0°C. The resulting dark mixture was added to a solution of NaOAc (1 g, 12 mmol), glacial acetic acid (4 mL) and **4.12** (800 mg, 4 mmol) in DMF (10 mL). The reaction mixture was stirred overnight at room temperature and poured in water (100 mL). The precipitate was collected, dried and recrystallized from EtOH giving **4.16** (150 mg, 8%) as dark red crystalline material.
Mp 196.8-198.5°C; ^{1}H-NMR (200 MHz): δ 3.21 (s, 3H), 4.71 (s, 2H), 6.84 (d, J=9.0, 2H), 7.25-7.37 (m, 5H), 7.92 (d, J=9.0, 2H), 8.00 (d, J=9.0 2H), 8.07 (d, J=9.0 2H), 8.10 (d, J=9.0, 2H), 8.41 (d, J=9.0, 2H); ^{13}C-NMR (75.3 MHz): δ 38.8, 56.2, 111.8, 123.1, 123.4, 124.4, 124.6, 125.6, 126.5, 127.2, 128.7, 137.6, 144.3, 148.7, 152.5, 152.5, 155.5, 155.9; UV/Vis: λ_{max}=504 nm (ϵ=4.51·10^4): HRMS calcd for $C_{26}H_{22}N_6O_2$: 450.180, found 450.180.

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